Evaporation of Cr_2O_3 in Atmospheres Containing H_2O

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ABSTRACT

Stainless steels in atmospheres containing H_2O form a Cr_2O_3 scale in the early stage of oxidation. However, the Cr_2O_3 scale gradually degrades with time. In order to determine the effect of H_2O on the deterioration of a Cr_2O_3 scale, evaporation behavior of Cr_2O_3 in N_2-O_2-H_2O atmospheres was investigated. The rate of mass loss in a N_2-O_2-H_2O atmosphere was found to be one order of magnitude higher than the rates in N_2-O_2 and N_2-H_2O atmospheres, indicating that deterioration of the Cr_2O_3 scale is likely to occur in mixed atmospheres of oxygen and water vapor. Volatilization of Cr_2O_3 is probably based on the following reactions: $1/2\ Cr_2O_3(s) + 3/4\ O_2(g) + H_2O(g) = CrO_2(OH)_2(g)$. However, it was also speculated that the reaction, $Cr_2O_3(s) + 3/2\ O_2(g) = 2\ CrO_3(g)$, affects the evaporation of Cr_2O_3 at temperatures higher than 1323 K. The evaporation rate of Cr_2O_3 is roughly comparable to the growth rate of the Cr_2O_3 scale. Therefore, a Cr_2O_3 scale can be degraded by the evaporation of Cr_2O_3.

Key words: High temperature oxidation, H_2O-Containing atmosphere, Evaporation of Cr_2O_3, Deterioration of Cr_2O_3 scale

1. INTRODUCTION

It is well known that oxidation of Fe-Cr alloys and stainless steels is accelerated in atmospheres

containing H_2O [1-2]. In the early stage of oxidation of these alloys, an oxide scale (Cr_2O_3 or Fe-Cr spinel oxide) is formed. Later, nodule-like oxides are formed locally, and then the alloy shows accelerated oxidation behavior, resulting in a large mass gain. In a hot-rolling process, such nodule-like oxides cause scale-related defects on the surface of the alloy because of the difficulty in removing them in the descaling process before hot rolling. We have investigated the initial oxidation behavior of several stainless steels at high temperatures in H_2O-containing atmospheres that modeled on heating conditions before hot-rolling processes, and our studies have clarified the effects of water vapor and content of Cr in stainless steels on the transition from an initial Cr_2O_3 scale to a nodule-like oxide [3-4]. However, the mechanism of the transition, that is, the cause of deterioration of a Cr_2O_3 scale by water vapor, has not been clarified.

Some mechanisms underlying the change from the initially formed Cr_2O_3 scale to a nodule-like oxide have been proposed. They can be classified into two main groups. One group concerns the deterioration of the mechanical property of a Cr_2O_3 scale [5-8]. That is, invasion of water vapor into the substrate is caused by deterioration of the mechanical property of the Cr_2O_3 scale accompanying the generation of cracks, which is due to dissolution of hydrogen into the Cr_2O_3 scale or to an originally brittle property of it. Jianian et al. [8] investigated the mechanism of breakaway oxidation in Fe-Cr alloys at 1173 K in wet oxygen, and they suggested that microchannels or microcracks in the initially formed Cr_2O_3 scale enabled $H_2O(g)$ to pass through the scale, resulting in the formation of nodule-like oxides and then the development of an external scale consisting of iron oxides (Fe_2O_3, Fe_3O_4) and an inner scale consisting of an Fe-Cr spinel oxide. The other group of possible mechanism concerns the reaction of a Cr_2O_3 scale with $H_2O(g)$ [9-15]. Asteman et al. [14-15] reported that evaporation of chromia occurred during oxidation of Type 304L at 873 K in humid oxygen. They showed that the evaporation of chromia, probably in the form of $CrO_2(OH)_2(g)$, resulted in the conversion of a Cr-rich oxide scale into a nonprotective iron-rich oxide scale.

As mentioned above, it is not still clear how an initially formed Cr_2O_3 scale changes into a nodule-like oxide, and little is known about the extent to which $Cr_2O_3(s)$ reacts with $H_2O(g)$. In the present study, reactions in atmospheres modeled on heating conditions before hot rolling were investigated. The evaporation behavior of Cr_2O_3 compacts in N_2-O_2-H_2O atmospheres was studied. Based on the results, the effect of water vapor on the deterioration of a Cr_2O_3 scale is discussed in this paper.

2. EXPERIMENTAL PROCEDURES

Cr_2O_3 compacts were fabricated by using a spark plasma sintering method. In this method, Cr_2O_3 powder (grain size of less than $5x10^{-6}$ m) was sintered at 1673 K. A high heating rate (10 K/s) and a compressive stress of 40 MPa in a graphite die were used for the sintering. The relative density of the sintered body was estimated to be about 95%, indicating a dense body. Specimens for the reaction tests were cut into 5x5x2($x10^{-3}$ m) blocks from the sintered Cr_2O_3 compact, and then the surfaces were polished up to a micrometer diamond finish. Prior to the reaction test, the specimens were ultrasonically cleaned in ethanol, and the mass and the surface area were measured.

The experimental apparatus used in this study was the same as that used in previous studies [3-4]. Reaction tests were carried out for up to 360 ks (100 hr) at 1173, 1273, 1323, 1373, and 1473 K in N_2-O_2, (N_2-O_2)-H_2O, and N_2-H_2O atmospheres. N_2-3%O_2, N_2-10%O_2, or N_2-20%O_2 mixed gas was used as a carrier gas to obtain N_2-O_2 and (N_2-O_2)-H_2O atmospheres, and the water vapor concentrations in the (N_2-O_2)-H_2O atmospheres were 6.9, 12.2, 19.7, and 45.4 vol.%. N_2 gas (purity: 99.999%) was used as a carrier gas to obtain an N_2-19.7%H_2O atmosphere. In the N_2-19.7%H_2O atmosphere, the maximum oxygen partial pressure is estimated to be about $1x10^{-5}$ atm O_2, assuming that impurity in the carrier gas, N_2, is oxygen only. Carrier gases with these H_2O concentrations were obtained by bubbling the N_2-O_2 mixed gas or the N_2 gas through distilled water maintained at 313, 323, 333, and 353 K. The flow rate was 2×10^{-4} m^3/min at room temperature.

For the reaction test, the specimen was quickly inserted into the hot zone of a reaction tube (internal diameter: 2.5×10^{-2}m) in an electric furnace maintained at a desired temperature and atmosphere. The specimen was heated for a desired time and then quickly removed from the hot zone and cooled in air. The reaction kinetics (evaporation behavior) was determined by measuring the difference in masses before and after heating.

3. RESULTS

3.1 Evaporation behavior of Cr_2O_3

Fig. 1 shows mass loss of Cr_2O_3 as a function of reaction time at 1173, 1273, 1323, 1373, and 1473 K in (N_2-3%O_2)-19.7%H_2O. The slight mass loss of Cr_2O_3 in the early stage of the reaction may be due to the roughness of the surface of specimen. After the early stage, a steady mass loss is observed at all

temperatures, probably due to smoothing of the surface of the specimen. The mass of Cr_2O_3 linearly decreases with reaction time at all temperatures. The slope of the line becomes larger with increase in temperature.

In order to determine the cause of the mass loss of Cr_2O_3, the specimens were heated at 1473 K in N_2-3%O_2, (N_2-3%O_2)-19.7%H_2O, and N_2-19.7%H_2O, and the mass losses of Cr_2O_3 in the three atmospheres were compared. The results are shown in Fig. 2. The mass losses in N_2-3%O_2 and N_2-19.7%H_2O are almost identical, and the values are small. This result shows that the partial pressure of the evaporating species is almost equal in the both environments. On the other hand, the mass loss in (N_2-3%O_2)-19.7%H_2O is quite large. This suggests that it is necessary to consider the evaporation of Cr_2O_3 based on the reaction in which both oxygen and water vapor participate.

Arrhenius plots of the evaporation rate of Cr_2O_3 in various atmospheres are shown in Fig. 3. The evaporation rate in the (N_2-3%O_2)-19.7%H_2O atmosphere is one order of magnitude higher than that in the N_2-3%O_2 and N_2-19.7%H_2O atmospheres. A change in the slope of the line in the (N_2-3%O_2)-19.7%H_2O atmosphere can be seen at a temperature around 1323 K, indicating that the evaporation mechanism of Cr_2O_3 changes at this temperature.

3.2 Effects of H_2O and O_2 concentrations

3.2.1 Effect of H_2O concentration

To determine the relationship between H_2O concentration and evaporation of Cr_2O_3 in N_2-O_2-H_2O atmospheres, the H_2O concentration in a carrier gas of N_2-3%O_2 was changed.

Fig. 4 shows the time dependence of the mass loss of Cr_2O_3 at 1473 K in (N_2-3%O_2)-X(=6.9,19.7,45.4)% H_2O atmospheres. As can be seen in the figure, the mass of Cr_2O_3 decreases linearly with time in all atmospheres, and the slopes of the lines are almost identical. In the same way, the mass losses were measured for carrier gases of N_2-10%O_2 and N_2-20%O_2. The rates of mass loss are shown in Fig. 5. In N_2-3%O_2, there is almost no dependence of rate of mass loss on H_2O concentration, while the rate of mass loss in N_2-10%O_2 and N_2-20%O_2 increases when the concentration of H_2O is 20% or more. The rate of mass loss also increases as the oxygen concentration increases.

3.2.2 Effect of O_2 concentration

The effect of O_2 concentration on mass loss of Cr_2O_3 was investigated in atmospheres with H_2O concentration fixed at 19.7%. Fig. 6 shows the time dependence of the mass loss at 1473 K in $(N_2\text{-}X\%O_2)\text{-}19.7\%H_2O$ (X=3,10,20) atmospheres. The mass loss decreases linearly with time in all atmospheres. The rate of mass loss becomes higher as the oxygen concentration increases. Such a tendency is also seen for various H_2O concentrations, as shown in Fig. 7. In all atmospheres, the rate of mass loss increases linearly as oxygen partial pressure increases. When the H_2O concentrations are 6.9% and 19.7%, the rates of mass loss are almost the same. However, the evaporation rate in the atmosphere with 45.4% H_2O is much higher than those in atmospheres with lower H_2O concentrations and strongly depends on oxygen concentration.

4. DISCUSSION

4.1 Reactions of Cr_2O_3 with O_2 and H_2O

A Cr_2O_3 scale is formed in the initial stage of the oxidation process in H_2O-containing atmospheres at high temperatures. However, the Cr_2O_3 scale gradually degrades with oxidation time, and finally a duplex structure consisting of external and inner scales is formed [3-4]. The external scale consists of iron oxides (Fe_2O_3, Fe_3O_4) and the inner scale consists of an Fe-Cr spinel oxide ($Fe(Fe, Cr)_2O_4$). In order to determine the effect of evaporation of Cr_2O_3 on deterioration of a Cr_2O_3 scale, the evaporation behavior of sintered Cr_2O_3 in various H_2O-containing atmospheres was investigated in this study. Based on the results, the reactions of Cr_2O_3 with O_2 and H_2O are discussed below.

Stearns [11] reported that the evaporation of Cr_2O_3 in O_2 atmospheres is caused by the following reaction:

$$Cr_2O_3(s)+3/2\ O_2(g)=2\ CrO_3(g). \qquad (1)$$

However, it is well known that the evaporation rates of Cr_2O_3 at temperatures below 1273 K are negligibly small [16]. The measurement of mass loss of Cr_2O_3 in an N_2-3%O_2 atmosphere in the present study also indicated that a measurable amount of Cr_2O_3 evaporated at temperatures higher than 1373 K. However, the evaporation rate in this atmosphere was one order of magnitude lower than that in the N_2-O_2-H_2O atmospheres. In addition, the evaporation behavior of Cr_2O_3 in the N_2-H_2O atmosphere was identical to that in N_2-3%O_2. Therefore, the evaporation as CrOOH, which is produced by the following reaction, can also be neglected at temperatures lower than 1373 K.

$$Cr_2O_3(s)+ H_2O(g)= 2\ CrOOH(g). \qquad (2)$$

Based on the above discussion, the evaporation of Cr_2O_3 is accelerated in the presence of both of oxygen and water vapor. Therefore, the evaporation of Cr_2O_3, which occurs by following reaction, would be predominant, as Ebbinghaus [13] calculated the partial pressures of various gaseous species from thermodynamic data for mixed atmospheres of O_2 and H_2O.

$$1/2\ Cr_2O_3(s) + 3/4\ O_2(g) + H_2O(g) = CrO_2(OH)_2(g). \qquad (3)$$

Now let us consider that the carrier gas, N_2, in N_2-19.7%H_2O contains minute amounts of oxygen. Assuming a gas composition of (N_2-0.001%O_2) -19.7%H_2O, equilibrium partial pressures of $CrO_2(OH)_2$ at 1373 and 1473 K are roughly in the order of 10^{-7} atm from calculations using the thermodynamic data provided by Ebbinghaus [13]. In a similar calculation, the equilibrium partial pressures of CrO_3 at 1373 and 1473 K are estimated to be identical to that of $CrO_2(OH)_2$ in (N_2-0.001%O_2) -19.7%H_2O. These results may explain the observed mass loss without assuming the formation of CrOOH.

Similarly the equilibrium partial pressures of $CrO_2(OH)_2$ in N_2-2.4%O_2-19.7%H_2O were calculated. The calculated pressure is three order of magnitude higher than that of $CrO_2(OH)_2$ in N_2 -19.7%H_2O. This result is in good agreement with the effect of O_2 concentration on the evaporation of Cr_2O_3 in the formation of Cr oxyhydroxide.

As another mechanism, Glemser and Müller [17], Johnson and Panas [18-19] proposed the evaporation based on the following reaction:

$$CrO_3(g) + H_2O(g) = CrO_2(OH)_2(g). \qquad (4)$$

As shown in Fig. 3, the mechanism of evaporation of Cr_2O_3 in the N_2-O_2-H_2O atmosphere changes at 1323 K. The evaporation of Cr_2O_3 at temperatures lower than 1323 K may be governed by reaction (3), while, according to reaction (4), the formation of $CrO_3(g)$ at higher temperatures may also strongly affect the evaporation of Cr_2O_3.

4.2 Deterioration of Cr_2O_3 scale

The effect of evaporation of Cr_2O_3 on deterioration of Cr_2O_3 scales on stainless steels in atmospheres containing H_2O is discussed below. Fig. 8 shows the estimated reductions in thickness of sintered Cr_2O_3 at temperatures of 1173, 1323, and 1473 K in N_2-2.4%O_2-19.7%H_2O. The reduction in thickness was calculated from the evaporation rate of sintered Cr_2O_3. For example, the estimated reduction in thickness of Cr_2O_3 at 1473 K is about 10^{-11}m/s. On the other hand, the growth rate of a Cr_2O_3 scale on Type 430 at 1473 K in N_2-3%O_2 is about 10^{-10}m/s [3-4], which was estimated under an assumption that the growth of a

Cr_2O_3 scale obeys a linear rate law. The slight difference in these rates suggests that the evaporation of Cr_2O_3 can not be neglected for the stable growth of a Cr_2O_3 scale. This is in agreement with the result of Asteman's study [14-15] showing that H_2O reduced the ability of stainless steel to maintain a protective Cr_2O_3 scale due to volatile species. Consequently, it can be concluded that evaporation of Cr_2O_3 has a strong effect on the deterioration of a Cr_2O_3 scale formed in the early stage of oxidation of stainless steels in N_2-O_2-H_2O atmospheres.

5. CONCLUSIONS

1. A large amount of Cr_2O_3 evaporation occurs in mixed atmospheres of O_2 and H_2O.
2. Cr_2O_3 evaporates linearly with time in N_2-O_2-H_2O atmospheres, and the evaporation rate of Cr_2O_3 depends on O_2 and H_2O vapor concentrations.
3. The mechanism of the evaporation of Cr_2O_3 changes at 1323 K.
4. The evaporation of Cr_2O_3 in O_2-H_2O atmospheres results in deterioration of a Cr_2O_3 scale.

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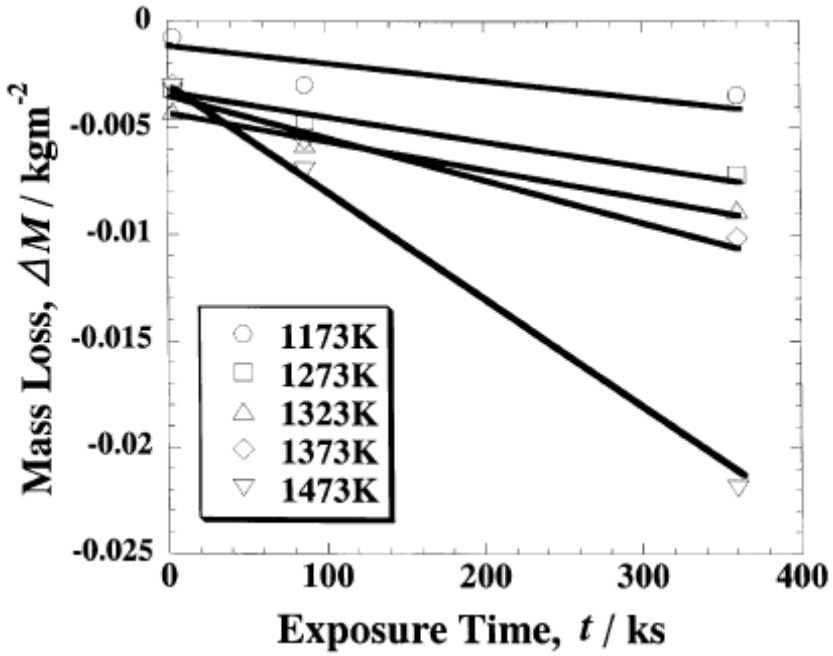

Fig. 1. Mass loss kinetics of Cr_2O_3 in N_2-2.4%O_2-19.7%H_2O atmospheres.

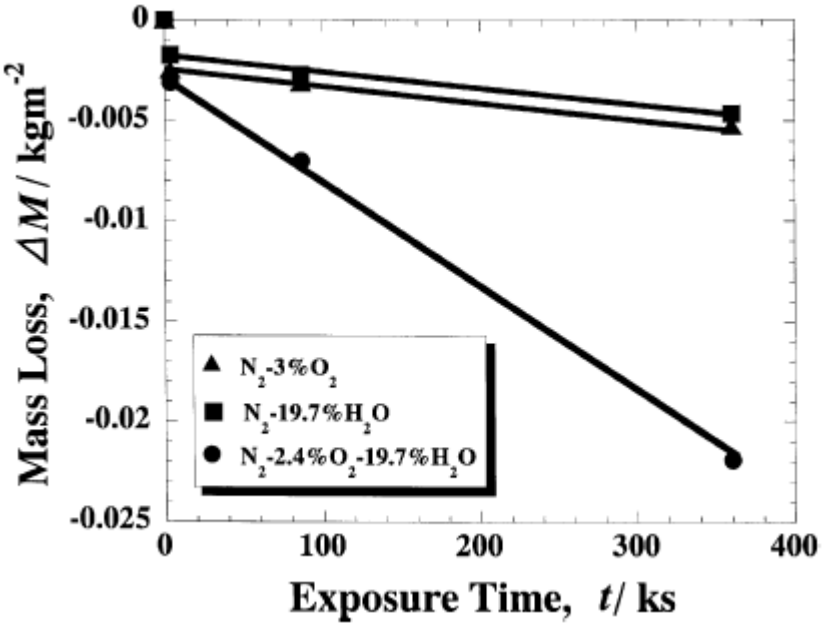

Fig. 2. Mass loss kinetics of Cr_2O_3 at 1473 K in N_2-3%O_2, N_2-19.7%H_2O, and N_2-2.4%O_2-19.7%H_2O atmospheres.

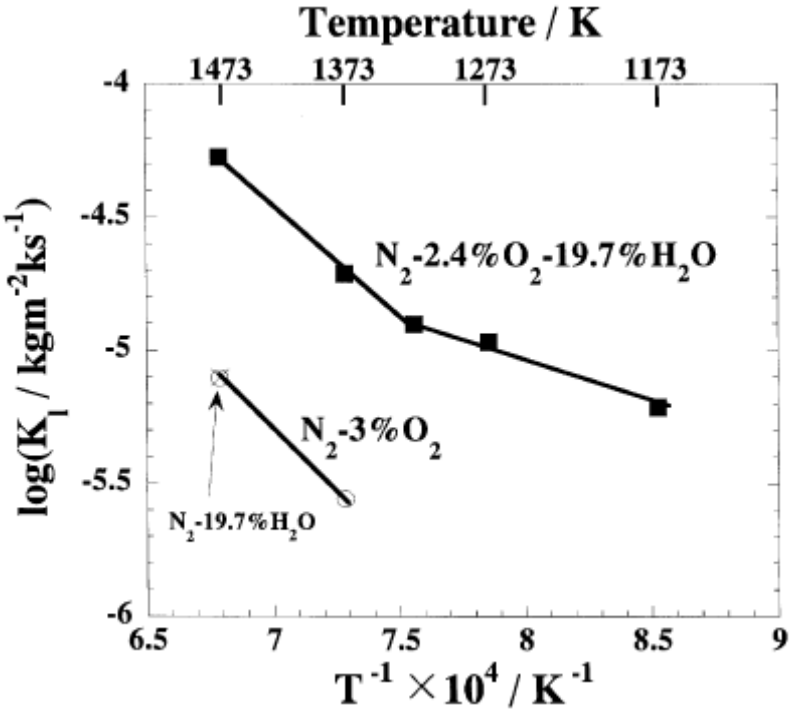

Fig. 3. Arrhenius plots of the evaporation rates of Cr_2O_3 in N_2-3%O_2 , N_2-19.7%H_2O and N_2-2.4%O_2-19.7%H_2O atmospheres.

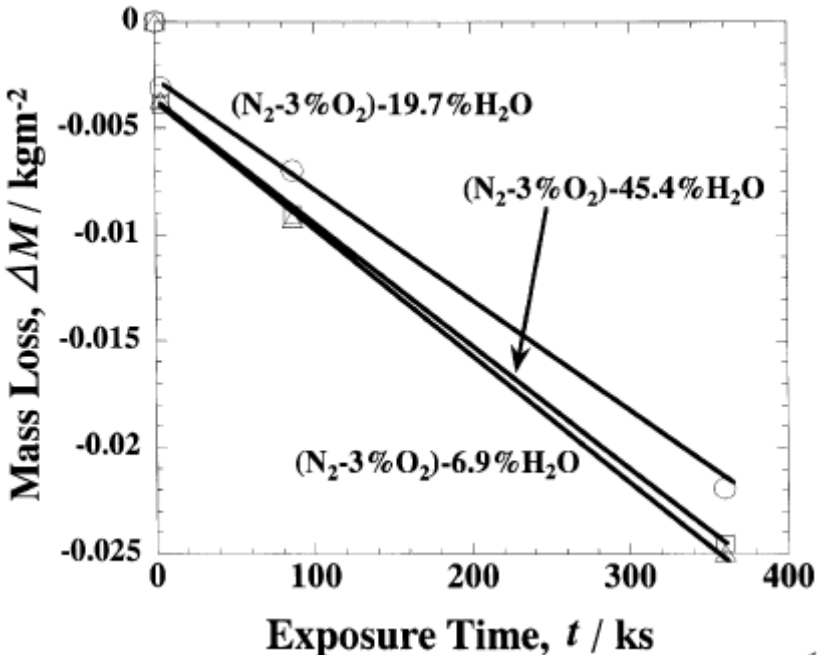

Fig. 4. Mass loss kinetics of Cr_2O_3 at 1473 K in (N_2-3%O_2)-X%H_2O (X=6.9, 19.7, 45.4%) atmospheres.

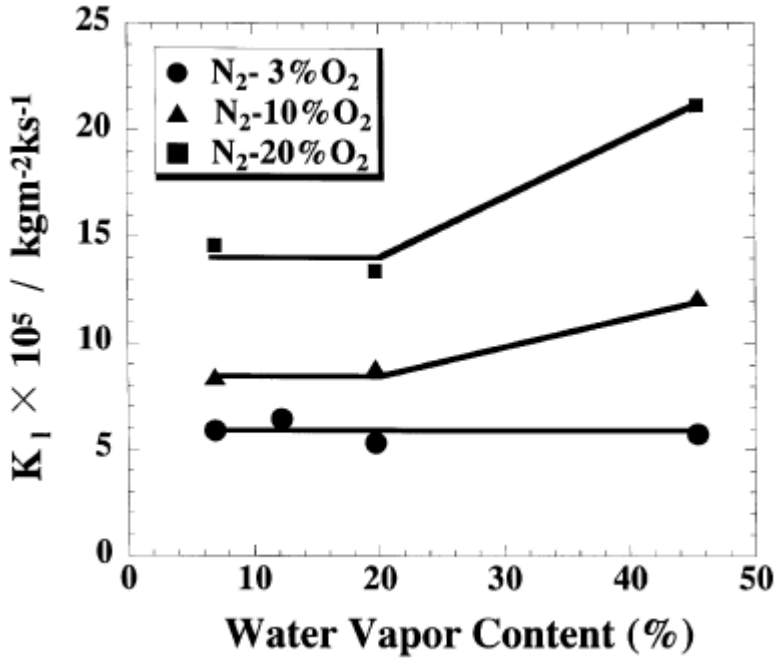

Fig. 5. Evaporation rate of Cr_2O_3 as a function of H_2O concentration at 1473 K in N_2-O_2-H_2O atmospheres.

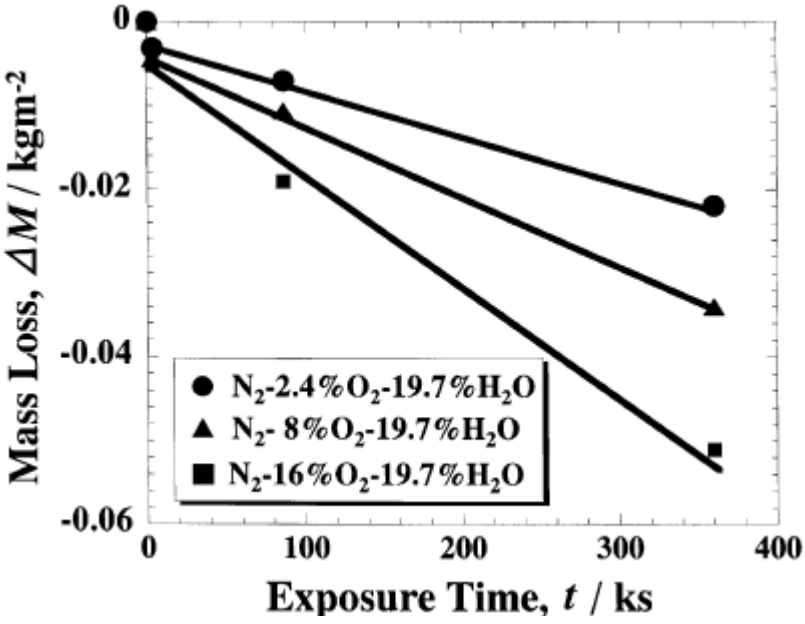

Fig. 6. Mass loss kinetics of Cr_2O_3 at 1473 K in (N_2-X%O_2)-19.7%H_2O (X=3, 10, 20%) atmospheres.

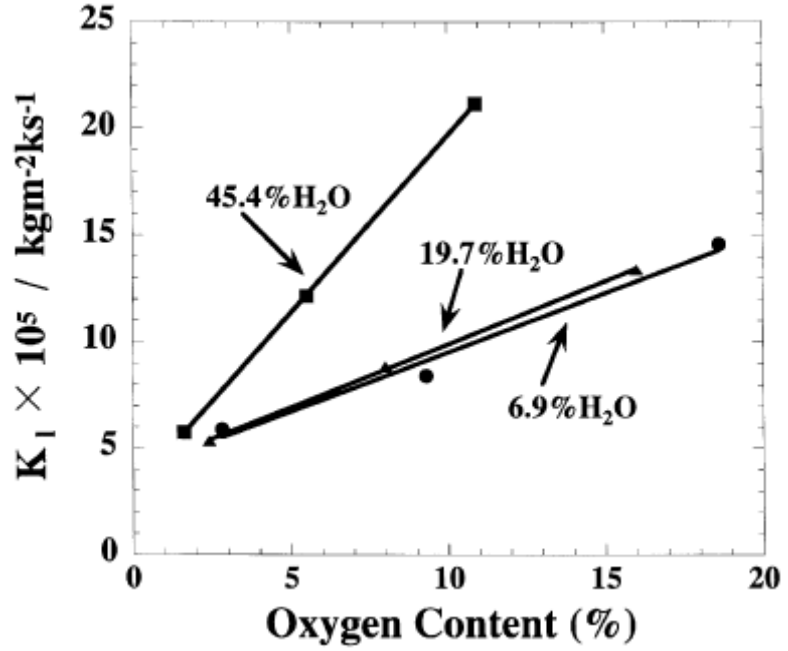

Fig. 7. Evaporation rate of Cr_2O_3 as a function of O_2 concentration at 1473 K in N_2-O_2-H_2O atmospheres.

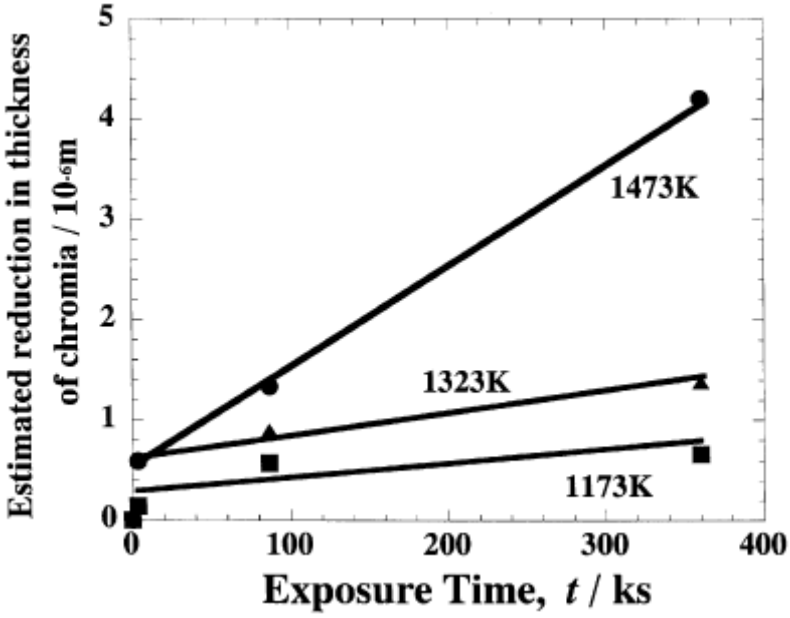

Fig. 8. Change in the estimated thickness of Cr_2O_3 with time at various temperatures in N_2-2.4%O_2-19.7%H_2O atmospheres.